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MAGNETIC PHASE TRANSITION OF $Li_{0.75}CoO_2$ COMPARED WITH $LiCoO_2$ AND $Li_{0.5}CoO_2$

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Magnetic and thermodynamic properties of the $LiCoO_2$ positive-electrode material used in lithium-ion battery were first examined. Partially deintercalated $LiCoO_2$, that is $Li_{0.75}CoO_2$, showed definite anomaly in the magnetic susceptibility at T = ca. 175 K probably related to magnetic phase transition which was supported by observation of a weak anomaly in heat capacity. On the other hand, $LiCoO_2$ did not show such magnetic phase transition as expected, whereas $Li_{0.5}CoO_2$ a weak one in the similar temperature range. These behaviors are discussed in association with the mixing of Co^{3+} and Co^{4+} electronic structures.

Keywords: Magnetic phase transition, $LiCoO_2$, Heat capacity, Electrochemical deintercalation

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Introduction

In recent years $LiCoO_2$ is used as the material for fabrication of the positive electrode in lithium-ion battery[1-3]. This comes from feasibility of this electrode, which could afford possible high efficiency of energy density (120-140 mAh/g), high cell voltage (ca. 4.1 V vs. Li), and structural robustness toward the reversible charging-discharging process for 500-1000 cycles. $LiCoO_2$ has a layered α-$NaFeO_2$ structure of the space group $R\bar{3}m$, where Li atoms are intercalated at the interlayer octahedral sites[3]. In the charged state of this material, Li atoms are electrochemically deintercalated out of the above structure normally down to the component of $Li_{0.5}CoO_2$ without causing serious damage to the original CoO_2 structure. Thus the Li amount in $Li_{1-x}CoO_2$ changes in the range $x = 0 – 0.5$, corresponding to, e. g., the cell voltage 0.5 – 4.5 V vs. Li electrode.

It is considered that, in $LiCoO_2$, Co is in the valence state of Co^{III} (namely Co^{3+}) with $3d^6$ low-spin characteristics. In accompany with deintercalation of Li, particularly in $Li_{0.5}CoO_2$, the Co^{IV} state (Co^{4+}) is supposed to become mixed. Hence it would be of interest to systematically examine the magnetic property of $Li_{1-x}CoO_2$. In this paper, the temperature-dependent magnetic susceptibility is studied with respect to three kinds of the $Li_{1-x}CoO_2$ samples (x = 0, 0.25, and 0.5) prepared by the electrochemical deintercalation procedure. Moreover, the heat capacity measurement is also performed to be related with magnetic susceptibility behavior.

Experimental

The samples were prepared as described in what follows: The high-grade $LiCoO_2$ powder sample was purchased from Kansai Catalyst Co., Ltd. and used without further purification. This source powder was mixed with graphite powder working as the electric conduction

mediator and poly(vinylidene fluoride) (PVdF) as the binder at the weight ratio of 100:5:3.5, respectively, to make paste-like stuff. Aluminum film was utilized as the back lead for thus prepared $LiCoO_2$ electrode and the whole electrode was finished in a sheet form of thickness of ca. 200 μm.

The deintercalation of Li from this electrode was performed in an electrochemical manner with constructing the three-electrode electrochemical cell in which for both the counter and the reference electrodes is used metallic lithium. The electrolyte was prepared with 1M $LiPF_6$ in rigorously dehydrated propylene carbonate (PC). The Li atoms in the $LiCoO_2$ electrode was deintercalated by charging in the usual electrochemical process to obtain the $Li_{0.75}CoO_2$ and $Li_{0.5}CoO_2$ samples in a coulometric control by using the charge-discharge unit (Hokuto HJ-201B) under the constant current (1.7 mA/cm^2) condition in an argon drybox. The electrode thus prepared was thoroughly washed with dimethoxyethane (DME) for twelve hours and dried in vacuum for one hour, and then the aluminum film was removed by peeling off.

Magnetic susceptibility was measured in the temperature range 5-300 K using a SQUID magnetometer (MPMS, Quantum Design) and the heat capacity measurement from 2-300 K (for $Li_{0.75}CoO_2$) and from 5-300 K (for $Li_{0.5}CoO_2$) using a relaxation type calorimeter (PPMS, Quantum Design). Note that the present electrode samples include contribution from PVdF (binder) and graphite (electric conduction mediator), since we examine the total behavior of the $Li_{1-x}CoO_2$ electrodes.

Results and discussion

Magnetic susceptibility

Temperature dependencies of magnetic susceptibility of the three kinds of $Li_{1-x}CoO_2$ electrode samples (x = 0, 0.25, and 0.5) are shown in Fig. 1. There is seen no obvious change in the sample with x = 0 (i.e., $LiCoO_2$) but for those with x =0.25 and 0.5 a certain anomaly is seen.

Details of this anomaly in these two samples are shown in the inset of Fig. 1, where $Li_{0.75}CoO_2$ shows a clear step with the center at 168.3 K and $Li_{0.5}CoO_2$ a little weaker step at 170.8 K. Hence for these two samples a heat capacity measurement is further performed to ascertain the magnetic anomaly, the result of which is described in the following.

Heat capacity

Figure 2 shows behavior of heat capacities of $Li_{0.75}CoO_2$ and $Li_{0.5}CoO_2$. It is seen that $Li_{0.75}CoO_2$ has a slight but definite step starting at 174.6 K and finishing at 165.5 K whereas $Li_{0.5}CoO_2$ has not. Thus $Li_{0.75}CoO_2$ electrode material shows the definite anomalies in both the magnetic susceptibility and the heat capacity in the temperature range 165-175 K.

It is rather hard to specify whether these anomalies are related to the first order or the second order phase transition, since the present material is considered to be far from crystalline structure and the anomaly peaks are rather smeared. Nonetheless, it is noted that even such material still shows measureable phase transition.

Spin states of Co^{III} and Co^{IV}

It has been well recognized that in $LiCoO_2$ the valence of Co (originally $3d^74s^2$) is mostly in the Co^{III} state (that is, Co^{3+}) and has diamagnetic $3d^6$ electronic structure. On the other hand, the Co^{IV} state (Co^{4+}) having paramagnetic $3d^5$ electronic structure becomes mixed. Hence in $Li_{1-x}CoO_2$ ($0 < x < 0.5$) there could appear a certain biphase magnetic property. In this sense, the

electronic structure of Co in $Li_{0.75}CoO_2$ may well have an interplay of $3d^6$ and $3d^5$ electronic structures, which will cause rather complicated behavior of electronic property depending on the structure (e.g., pure crystalline, polycrystalline with grain boundary, and so on).

Electrical transport measurements by Ménétrier et al. have concluded semiconductive behavior of $LiCoO_2$ and metallic behavior of $Li_{1-x}CoO_2$ for $x \geq 0.3$ [4], although it had been controversial about the origin of the electric conduction carriers [5,6]. These are well understood that the diamagnetic Co state is dominant in $LiCoO_2$ to bring about semiconductive behavior, whereas at $x \geq 0.3$ the contribution from the open-shell structure of Co^{4+} starts to contribute to eventual electric conduction.

Moreover, it has also been found that in $Li_{0.70}CoO_2$ there is a metal-insulator transition at 175 K, that is, $Li_{0.70}CoO_2$ shows metallic behavior between 300-175 K but not under 175 K[4]. This fact can be related with temperature dependence of the interplay between Co^{IV} and Co^{III} in $Li_{0.70}CoO_2$ itself and that this metal–insulator transition is obviously associated with spin change from the high-spin to the low-spin state due to the temperature decrease in $Li_{0.70}CoO_2$ at 175 K. The spin-state change thus observed in ref. 4 will be parallel to our present observation of magnetic phase transition and heat capacity anomaly in $Li_{0.75}CoO_2$ in the similar temperature range.

There can be at least two possibilities for the magnetic phase transition: (i) a spin dimerization of Co^{IV} takes place in some sense to cancel out the high spin-state and, hence, the conduction carrier decreases as well at T = ca. 175 K, and (ii) the amount of Co^{IV} decrease to change into Co^{III} upon temperature change. Although it is currently yet unclear which of these two is plausible to occur in the actual system, it can be said that there is a subtle magnetic transition in $Li_{1-x}CoO_2$ in the course of Li deintercalation which requires further study.

$Li_{0.5}CoO_2$ also showed similar but weaker magnetic phase transition, whereas such behavior was not apparent in the heat capacity measurement. This signifies that interplay of high-spin and low-spin states is less remarkable in $Li_{0.5}CoO_2$.

Conclusion

Magnetic phase transition has been examined in $Li_{1-x}CoO_2$ electrode material samples (x = 0, 0.25, and 0.5) prepared by electrochemical deintercalation procedure. Possible magnetic phase transition from the high-spin to the low-spin state in $Li_{0.75}CoO_2$ has been found out at T = ca. 175 K. The anomaly found in heat capacity measurement at the similar temperature range supports this aspect. This phase transition has been discussed in association with metal-insulator transition previously reported.

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References

1 K. Mizushima, P. C. Jones, P. J. Wiseman and J. B. Goodenough, Mat. Res. Bull., 15 (1980) 783.

2 Y. M. Choi, S. I. Pyun, J. S. Bae and S. I. Moon, J. Power Sources, 56 (1995) 25.

3 T. Ohzuku and A. Ueda, Solid State Ionics, 69 (1994) 201.

4 M. Ménétrier, I. Saadoune, S. Lavasseur and C. Delmas, J. Mater. Chem., 9 (1999) 1135.

5 A. Honders, J. M. der Kinderen, A. H. van Heeeren, J. H. W. de Witt and G. H. J. Broers,

Solid State Ionics, 14 (1984) 205.

6 J. Molenda, A. Stoklosa and T. Bak, Solid State Ionics, 36 (1989) 53.

Figure captions

Fig. 1 Magnetic susceptibility change for $Li_{1-x}CoO_2$ (x = 0, 0.25, and 0.5) electrode materials. The inset shows a detailed data for those of $Li_{0.75}CoO_2$ and $Li_{0.5}CoO_2$.

Fig. 2 Heat capacity change for $Li_{0.75}CoO_2$ and $Li_{0.5}CoO_2$ electrode materials.

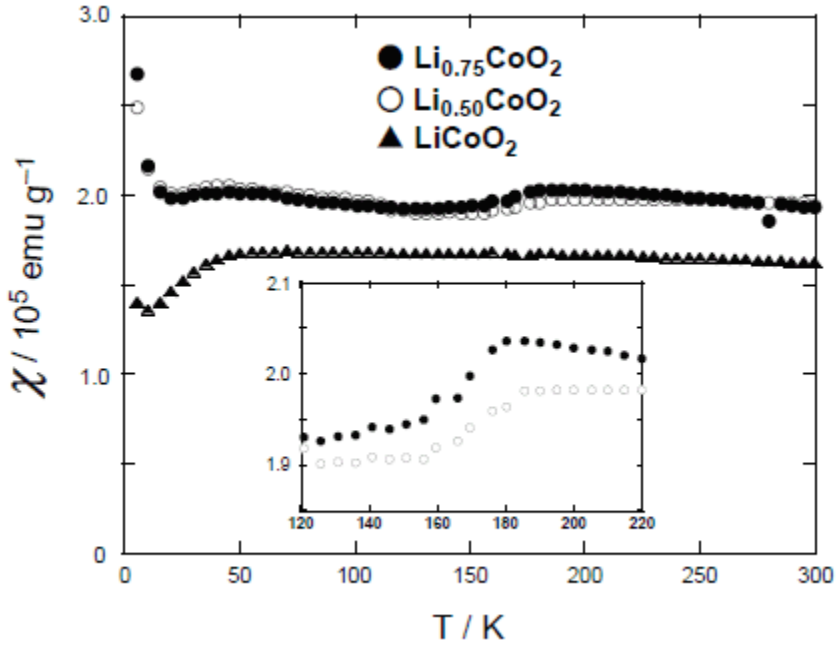

Fig. 1

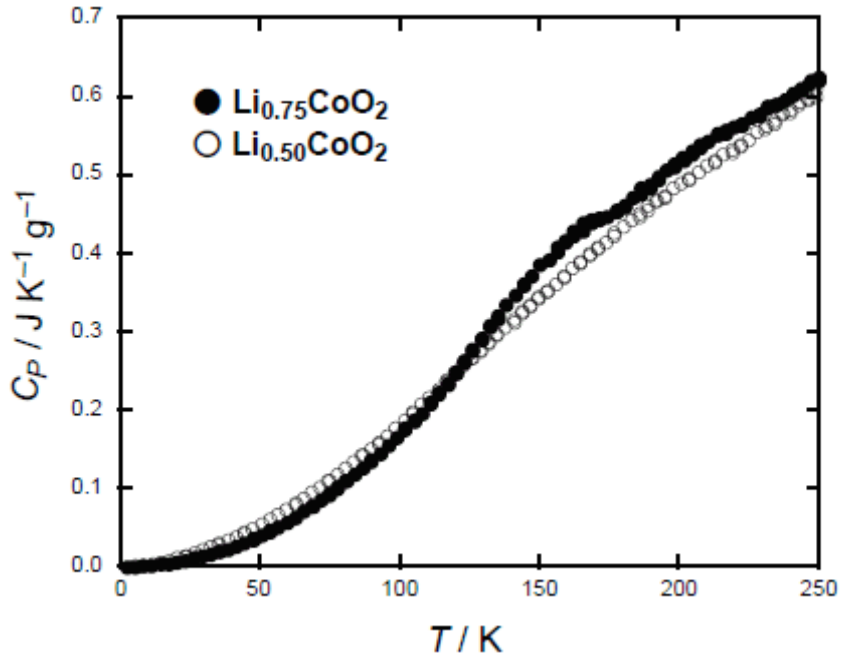

Fig. 2